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Kiil, Søren

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# Quantitative analysis of pigment dispersion taking into account the full agglomerate size distribution

Søren Kiil\*

\*Department of Chemical and Biochemical Engineering, Technical University of Denmark, DTU,  
Building 229, DK-2800 Kgs. Lyngby, Denmark, Email: sk@kt.dtu.dk

## *Abstract*

*This work concerns the development of simulation tools for mapping of pigment dispersion. Focus has been on the mechanical breakage of pigment agglomerates. The underlying physical mechanism was assumed to be surface erosion of spherical pigment agglomerates, and the full agglomerate particle size distribution was simulated. Data from previous experimental investigations with organic pigments were used for model validation. When the linear rate of agglomerate surface erosion was taken to be proportional to the external agglomerate surface area, simulations of the volume-moment mean diameter over time were in good quantitative agreement with experimental data. The only adjustable parameter used was an apparent rate constant for the linear agglomerate erosion rate. Model simulations, at selected values of time, for the full agglomerate particle size distribution were in good qualitative agreement with measured values. The general applicability of the model, beyond the pigments considered, needs to be confirmed.*

## **Introduction**

When pigments are manufactured, the targeted particle size distribution (PSD) will reflect the best compromise of particle properties. However, the individual particles will typically, due to van der Waals forces (i.e. physical interactions) and despite various surface treatments, be present in porous agglomerates in the final pigment powder. During subsequent coating or ink production, the agglomerates need to be taken apart to smaller entities in an attempt to optimize coating properties such as color strength and shade, opacity and hiding power, UV radiation resistance, gloss, and rheology [1,2]. This process is called “dispersion” and is one of the most important steps in the production of pigmented coatings or inks. Dispersion is done with a so-called “mill base” (where no particles are actually “milled”), which consists of pigment powders in one or more viscous binder components, often also including dispersion agents and some solvent. The dispersion obtained is subsequently mixed with other ingredients to form the final coating.

The dispersion process itself is complex and consists of three separate steps: wetting of pigment surfaces, mechanical disruption (breakage) of agglomerates, and stabilization of the primary particles (or smaller agglomerates) formed, to prevent reagglomeration. From a practical point of view, pigment dispersion must be an efficient process. This means that machine power consumption should be minimized and/or dispersion time kept as low as possible. Which type of equipment to use depends on the pigments of interest (agglomerate strength) and typically coating companies will have more than one apparatus type available in house. Classical dispersion equipment, such as bead, ball, and pearl mills, high speed impellers, and roller mills are still extensively used, but also equipment based on new principles of dispersion have been introduced. Vacuum feeding of pigment powders (to remove air in agglomerates), breaking of large agglomerates with mechanical forces under dry conditions, and subsequent fast contact between agglomerates and wetting liquid under pressure are examples in this direction. Also, so-called rotor-stator principles are used, where high shear forces are generated in a workhead or a narrow gap.

The purpose of the present work was to develop a mathematical model that, based on a mechanistic understanding, quantifies the dispersion of pigments (or more precisely, the mechanical breakage of agglomerates), while taking into account the entire agglomerate PSD. An important requirement of this engineering model is that it should be sufficiently simple to allow daily use on dispersion processes. Simulations with the model are compared to previous experimental investigations of dispersion processes with selected organic pigments.

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## Mathematical model

The mathematical model was presented and verified against experimental data for organic pigments in a recent publication [2] and here will be given a concise, (almost) equation-free introduction. Only liquid dispersion, of relevance for coatings and inks, is considered. The model is capable of estimating the PSD development over time using a population balance approach. The underlying mechanism is illustrated in Fig. 1.

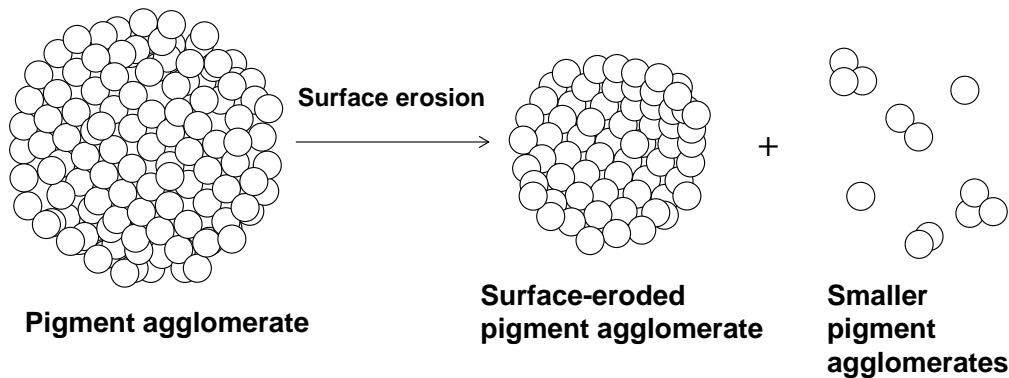


Figure 1: Schematic illustration of the mechanical disruption step in a pigment dispersion, where pigment agglomerates are reduced in size by surface erosion. Smaller agglomerates, in a distribution of sizes, are formed as erosion fragments. After [2].

The rate of agglomerate surface erosion was assumed proportional to  $d_{p,j}^n$  and expressed as

$$-\frac{d(d_{p,j})}{dt} = k_d d_{p,j}^n \quad (1)$$

where  $d_{p,j}$  is the current agglomerate diameter ( $j$  runs over all particle classes considered),  $k_d$  is a rate constant,  $t$  is time, and  $n$  the rate order (equal to 0, 1, 2, or 3).  $k_d$  is a function of the type of pigment agglomerates (e.g. porosity, cohesion strength, and primary particle shape), vehicle and dispersion equipment considered, pigment concentration in the vehicle, presence of dispersing additives and moisture, as well as operation parameters selected for a given dispersion experiment. A Rosin-Rammler distribution was assumed for the erosion fragments and used to distribute the fragments to smaller particle classes.

## Results and Discussion

The present version of the model is capable of estimating the particle size distribution development over time. As an example, in this short communication, the effects of erosion kinetics on dispersion for a yellow organic pigment (B3L) are investigated. Simulations and experimental data are compared in Fig. 2 (bottom plot). Both the dependency of the linear erosion rate on agglomerate diameter,  $n$ , and the erosion rate constant,  $k_d$ , were varied in an attempt to obtain the best possible agreement. The exponent  $n$  was varied only as  $n=0, 1, 2, 3$ . The first case ( $n=0$ ), corresponds to a constant and identical linear erosion rate for all agglomerates, whereas  $n=1, 2, 3$  corresponds to an agglomerate diameter-dependent, an external surface area-dependent, and a volume-dependent linear erosion rate, respectively. The erosion rate constant was allowed to vary freely. It can be seen in Fig. 2 (bottom plot) that  $n=0$  and  $n=1$  give simulations quite far from the experimental data. Initially, the simulated erosion rates are too slow, whereas at long dispersion times the rate of dispersion levels off with a lower mean agglomerate diameter in the simulations compared to experimental data. When  $n=3$ , the initial rate is somewhat too high and at long times the simulation converges to a mean agglomerate value higher than the experimental. Initially, when many large agglomerates are present,  $n=3$  will lead to a too high erosion rate, but as the agglomerates get smaller, the erosion rate will die out rapidly due to the high value of  $n$ . For  $n=2$ , the simulation (solid line) is in very good agreement with experimental data. It was assumed in the model that the dominating mechanism of dispersion is surface erosion, and  $n=2$  actually corresponds to an external surface area dependency of the rate.

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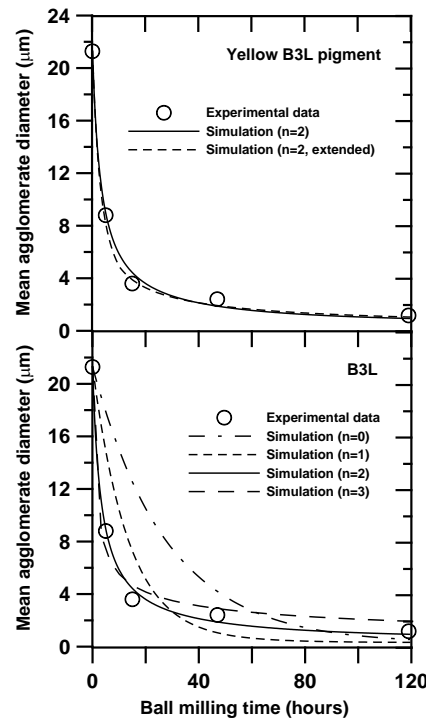


Fig. 2 Volume-moment mean diameter,  $D[4,3]$ , as a function of ball milling time for Pigment Yellow B3L pigment. The bottom plot shows the effect of the rate order,  $n$  ( $k_d$  is allowed to vary for each value of  $n$ ). The top plot shows the effect of using one, as opposed to several adjustable parameters. After [2].

The next issue to consider is how well the full PSDs are estimated when using  $n=2$  and the associated value of  $k_d$  from Fig. 2 (bottom plot). In Fig. 3 and 4, simulations (full lines) are compared to experimental data for four values of dispersion time (notice the logarithmic x-axis).

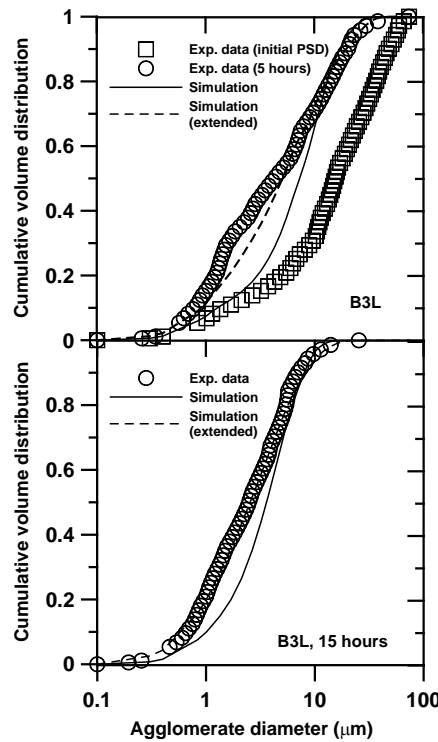


Fig. 3 Comparison of simulations and experimental data for two values of dispersion time (5 and 15 hours) for B3L pigment. In the top plot, also the initial PSD, which serves as an input to simulations, is shown. In all simulations shown,  $n=2$ . The solid lines represent simulations when using only one adjustable parameter ( $k_d$ ). The dashed lines are simulations where several adjustable parameters were used. After [2].

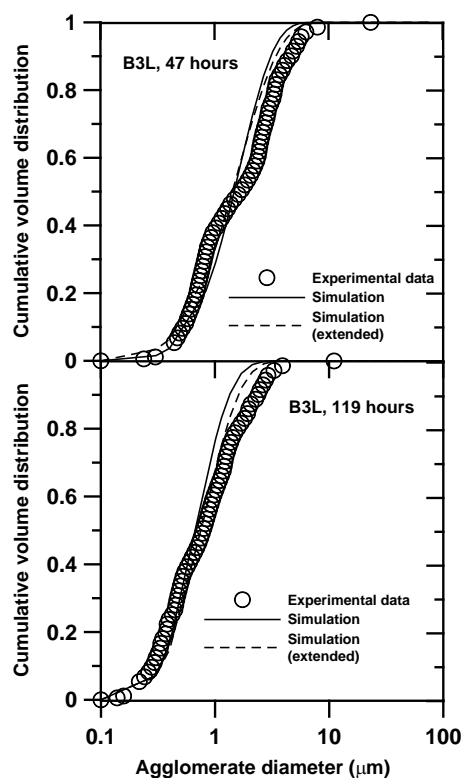


Fig. 4 Comparison of simulations and experimental data for two values of dispersion time (47 and 119 hours) for B3L pigment. In all simulations shown,  $n=2$ . The solid lines represent simulations when using only one adjustable parameter ( $k_d$ ). The dashed lines (“extended”) are simulations where several adjustable parameters were used. After [2].

Starting with Fig. 3, representing “snapshots” after 5 and 15 hours of dispersion, respectively, it can be seen that the large particle sizes from 100 down to about 10  $\mu\text{m}$  are in good agreement with experimental data. However, particles smaller than about 10  $\mu\text{m}$  are not predicted very well. In Fig. 4, showing “snapshots” after 47 and 119 hours of dispersion, the agreement is good for the small particles, but less good for the “large” particles (at this point in dispersion time between about 1 and 10  $\mu\text{m}$ ). It is interesting that, despite the good agreement for all values of time in Fig. 2, the full PSDs are not quantitatively described. This can be attributed to the data in Fig. 2 being mean values, where deviations for the smallest agglomerates will not weigh to any great extent in the calculations. This was further verified by conducting a modified simulation (“extended”), where more model parameters were allowed to vary. It was chosen to let the distribution of eroded fragments from each agglomerate have a characteristic particle size three times smaller than the arithmetic mean value used in the Base Case for the first 10 hours of the dispersion experiment. The modified simulation is shown with dashed lines in Fig. 2 (top plot) and Fig. 3 and 4. It is evident that a better match is obtained for the full PSDs, but also that the effect on the mean agglomerate diameter (Fig. 2, top) is quite small.

## Conclusions

The mathematical model developed in [2] is able to simulate experimental data available for selected organic pigments. In the presentation, a range of simulations with the model will be shown and discussed. Future work with the model involves extension to other types of pigments (e.g. inorganic pigments).

## Acknowledgement

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## References

- [1] Winkler, J., Dispersing pigments and fillers, Hannover, Germany, Vincentz, 2012.
- [2] Kiil, S., Mathematical modelling of pigment dispersion taking into account the full agglomerate particle size distribution, JCT Research, Accepted May 2016, In Press.